STATIC AND DYNAMIC MECHANICAL PROPERTIES AND STRAIN RATE SENSITIVITY OF THERMOPLASTIC BASED POLYMERS AND COMPOSITES USING SPLIT HOPKINSON PRESSURE BAR APPARATUS

by

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Doctor of Philosophy

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled " Static And Dynamic Mechanical Properties And Strain Rate Sensitivity Of Thermoplastic Based Polymers And Composites Using Split Hopkinson Pressure Bar Apparatus ". I also declare that it has not been previously submitted for the award for any degree or diploma or other similar title for any other examining body or university.

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LIST OF SYMBOLS

$\dot{\varepsilon}$	Strain rate
ΔH_m	Melting Heat of The Sample
ΔH_0	Melting Heat of 100% Crystalline Thermoplastic
ω	Test Frequency
V^*	Thermal Activation Volume
ρ	Density
δ	Tan Delta
θ	Bragg Angle
"k"	Number of Wave Cycles
A_b	Cross-Sectional Area of Bar
A_s	Cross-Sectional Area of Specimen
C_o	Wave Velocity
d_{hkl}	Distance Between Adjacent Planes
d_o	Displacement Amplitude
E	Bridge Voltage
E	Young Modulus
E'	Storage Modulus
E''	Loss Modulus
e_o	Voltage Change In The Bridge
G	Amplifier Gain Factor
k	Boltzmann Constant
l_g	Specimen Gauge Length
l_o	Initial Length of The Specimen
n	Interger Number
s_g	Strain Gage Factor
T	Absolute Temperature
V	Mechanical Impedance Value
v	Velocity of Deformation
β	Strain Rate Sensitivity Parameter

ε	Strain Pulse
ε_i	Incident Strain Pulse
ε_r	Reflected Strain Pulse
ε_t	Transmitted Strain Pulse
λ	Wavelength of X-ray Beam
σ	Stress
$\sigma_{average}$	Average Stress
σ_{back}	Back Stress
σ_{front}	Front Stress
σ_i	Internal Stress
σ_y	Yield Stress

LIST OF ABBREVIATIONS

ABS	Acrylonitrile Butadiene Styrene
ASTM	American Society For Testing and Materials
$CaCO_3$	Calcium Carbonate
CMCs	Ceramic Matrix Composites
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calometry
EDX	Energy Dispersive X-ray
FESEM	Field Emission Scanning Electron Microscopy
FT-IR	Fourier Transform Infrared Spectroscopy
GFRC	Glass Fiber Reinforced Composite
HDPE	High Density Polyethylene
HRTEM	High Resolution Transmission Electron Microscopy
KBr	Potassium Bromide
LDPE	Low Density Polyethylene
LLDPE	Linear Low-Density Polyethylene
MMCs	Metal Matrix Composites
PA-6	Nylon 6
PA-66	Nylon 66
PC	Polycarbonate
PE	Polyethylene
PEEK	Polyether Ether Ketone
PET	Polyethylene Terephthalate
PFTCs	Particulate Filled Thermoplastic Composites
PMCs	Polymer Matrix Reinforced Composites
PMMA	Polymethyl Methacrylate
POM	Polyoxymethylene
PP	Polypropylene
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl Chloride

SHPBA	Split Hopkinson Pressure Bar Apparatus
SiO_2	Silica
TGA	Thermogravimetric Analysis
UCS	Ultimate Compressive Strength
UHMWPE	Ultra High Molecular Weight Polyethylene
UTM	Universal Testing Machine
XRD	X-ray Diffraction
ZnO	Zinc Oxide

SIFAT-SIFAT MEKANIKAL STATIK DAN DINAMIK DAN KEPEKAAN KADAR TERIKAN BAGI POLIMER BERASASKAN THERMOPLASTIK DAN KOMPOSIT MENGGUNAKAN ALAT PECAHAN HOPKINSON TEKANAN BAR

ABSTRAK

Dalam kajian ini, teknik eksperimen, berasaskan pemampatan pecahan Hopkinson tekanan bar (SHPB), telah diperkenalkan untuk menjalankan ujian mampatan dinamik manakala mesin ujian konvensional sejagat telah digunakan untuk menjalankan ujian mampatan statik. Kedua-dua teknik digunakan untuk secara eksperimennya menyiasat kesan interaktif kadar terikan terhadap sifat-sifat mampatan pelbagai bahan berasaskan termoplastik. Semua bahan-bahan berasaskan termoplastik yang digunakan dalam kajian ini telah dihasilkan menggunakan proses penekanan panas. Keputusan SHPB pada awalnya telah disahkan dan ditentukur. Hasil kajian menunjukkan bahawa semua spesimen termoplastik yang diuji (iaitu PP, PE, dan PC) mempamerkan pergantungan besar pada kadar terikan yang dikenakan; dimana tegasan alah, modulus mampatan dan kekuatan mampatan, semuanya telah meningkat dengan peningkatan kadar terikan. Menariknya, kedua-dua persamaan Eyring dan persamaan hukum kuasa asas hampir selari dengan keputusan uji kaji bagi keseluruhan kadar terikan yang disiasat. Kesan struktur molekul, terhadap sifat-sifat mekanikal statik dan dinamik bagi termoplastik polimer, juga telah ditentukan menggunakan spesimen polietilena dengan struktur molekul yang berbeza (iaitu LDPE, LLDPE and HDPE). Keputusan menunjukkan bahawa struktur molekul polietilena telah memberi kesan kepada sifat-sifat mekanikal dari segi takat alah, kekakuan, kekuatan, kadar kepekaan, isipadu pengaktifan, dan tenaga yang diserap.

Bagi komposit berasaskan termoplastik, dua jenis partikel pengisi telah ditambah ke dalam matrik polipropilena; iaitu zink oksida dan mika. Ia boleh dilihat secara jelas bahawa pengenalan pengisi meningkatkan sifat-sifat mampatan komposit, termasuk modulus mampatan, serta kekuatan alahnya. Kajian juga telah mendapati bahawa kandungan partikel mempamerkan hubungan yang tidak ketara dengan sensitiviti kadar tekanan dan isipadu haba pengaktifan, bagi kedua-dua polipropilena diperkuat sistem komposit. Bagi kesan ciri-ciri partikel-matrik, serbuk partikel silika telah dimanipulasi untuk menyiasat secara eksperimen mengenai hubungan antara saiz partikel dan sifat-sifat mekanikal komposit di bawah pelbagai kadar terikan yang di kenakan. Menariknya, saiz partikel-partikel silika memberikan kesan yang jelas ke atas sifat-sifat mampatan komposit berasaskan polipropilena. Secara kuantitatifnya, komposit dengan silika bersaiz nano mencatatkan sifat-sifat mampatan yang lebih tinggi, dari segi kekuatan alah, kekuatan muktamad dan kekakuan berbanding komposit dengan silika besaiz mikro, untuk semua kadar terikan yang di siasat.

STATIC AND DYNAMIC MECHANICAL PROPERTIES AND STRAIN RATE SENSITIVITY OF THERMOPLASTIC BASED POLYMERS AND COMPOSITES USING SPLIT HOPKINSON PRESSURE BAR APPARATUS

ABSTRACT

In this study, an experimental technique, based on the compression Split Hopkinson Pressure Bar (SHPB), was introduced to perform dynamic compression testing whereas a conventional universal testing machine was used to perform static compression testing. These two techniques were used to experimentally investigate the interactive effect of strain rates towards the compressive properties of various thermoplastic-based materials. All of the thermoplastic-based materials used in this study were fabricated using a hot press process. The SHPB results were initially verified and calibrated. The results indicated that all tested thermoplastic specimens (i.e. PP, PE, and PC) showed a great dependency on the strain rate applied; where the yield stress, compression modulus, and compressive strength, were all proportionally increased as the strain rate was increased. Interestingly, both Eyring and basic power law equations were almost agreed with the experimental results over a wide range of strain rates investigated. The effect of molecular structure, on the static and dynamic mechanical properties of thermoplastic polymer, was also determined using polyethylene specimens with different molecular structures (i.e. LDPE, LLDPE, and HDPE). The results indicated that the molecular structure of polyethylene did affect its mechanical properties in terms of yield behaviour, stiffness, strength, rate sensitivity, activation volume, and absorbed energy. For thermoplastic based reinforced composites, two types of particulate fillers were added into the polypropylene matrix namely zinc oxide and mica. It can be clearly seen that the

introduction of filler increased the composites' compressive properties, including their compression modulus, as well as their yield strength. It was also found that the particle content showed an insignificant relationship with strain rate sensitivity and thermal activation volume, for both polypropylene reinforced composite systems. As for the effect of particle-matrix characteristics, silica particles were manipulated to experimentally investigate the correlation between particle size and the mechanical properties of composites under a wide range of strain rates investigated. Interestingly, the size of the silica particles gave significant effects on the compressive properties of the polypropylene-based composites. Quantitatively, composites with nano-sized silica recorded higher compressive properties, in terms of yield strength, ultimate strength and stiffness as compared to composites with micro-sized, for all strain rates investigated.

CHAPTER 1

INTRODUCTION

1.1 Static and dynamic mechanical properties of materials

The mechanical performance of materials is determined by their static and dynamic mechanical characteristics. Unfortunately, the majority of scientists only focus on the static rather than on the dynamic mechanical behaviour of materials. This is attributed to the limited number of dynamic facilities, as well as the difficulty in performing dynamic testing. Intensive efforts should be carried out in the future in order to gain a better understanding of the dynamic perspective of the behaviour of materials.

1.2 Development of dynamic testing

The knowledge of the characteristics of a material at dynamic loading is becoming ever more essential with the desire to produce products or structures that are capable of withstanding high velocity impacts. Based on this, several conventional mechanical tests have been developed over the years to obtain the mechanical characteristics of materials at high strain rates, using screw or hydraulic loading systems (Hamouda and Hashmi, 1998; Field et al., 2004). For example, a pendulum impact machine, such as the Charpy or Izod, can yield a strain rate of up to 100 s^{-1}, but only provide the absorbed energy information up to fracture. Meanwhile, other common high strain rate facilities are the drop-weight impact and the servo-hydraulic tester. Although a drop-weight impact test can give both impressive and

convenient results, but the test is still limited by several factors, such as the sensitivity towards contact conditions between the impactor and the specimen (Hsiao et al., 1999). In addition, the drop-weight test is also restricted to lower strain rate conditions (i.e. between 1 to 10 ms^{-1}) (Richardson and Wisheart, 1996). On the other hand, the servo-hydraulic test also has a similar restriction with the drop-weight impact test, where it is only credible for intermediate strain rates (Othman et al., 2009).

A desire to scrutinize the characteristics of materials at very high strain rates revealed a most promising technique, namely the Split Hopkinson Pressure Bar (SHPB) technique. The SHPB technique was initiated by Kolsky (1949) and developed by Hauser (1966), where a stress pulse travelled through an elastic input bar, through a short sample, and finally into an elastic output bar. The important characterisation of the SHPB technique is that it is highly dependent on the capability of the technique to obtain a stress–strain curve as the output, which holds useful information as to the characteristics of materials. Even though Kolsky introduced this technique almost five decades ago, it was only intensively used by researchers during the early 1970s. More recently, the SHPB technique has become the standard method for measuring the dynamic mechanical properties of materials in the range of 10^2 s^{-1} to 10^4 s^{-1} strain rates. (Evora and Shukla, 2003; Field et al., 2004). In the SHPB set-up, a semiconductor strain gauge is mounted on each Hopkinson bar. Meanwhile, the stress and strain within the specimen are obtained from an analysis of the signals from these two gauges. One of the basic and fundamental assumptions of the SHPB technique is the stress homogeneity within the sample. The technique assumes that the stress field is homogenous within the sample and that the propagating waves in

the bar have a negligible attenuation and dispersion. However, a conventional SHPB is not suitable for low impedance materials, such as polymers, polymeric foams and rubbers, because the transmitted signal is too small to be captured by the strain gauge mounted on the transmitter bar (Song and Chen, 2005; Van Sligtenhorst et al., 2006). Besides that, the equilibrium state is reached slowly when testing soft materials. Based on this limitation, the conventional theory of the SHPB technique will be invalid, and other solutions must be found. Lately, two common approaches have emerged to overcome this dilemma. In the first method, the application of a pulse shaper was used to induce a faster dynamic equilibrium achievement (Frew et al., 2005; Vecchio and Jiang, 2007). On the other hand, the second method was to use a low-impedance pressure bar, e.g. a polymer bar, which has an impedance value closer to that of the materials being tested (Johnson et al., 2010). It is believed that a closer impedance mismatch will significantly enhance the propagation of the transmitted pulse. Based on this concern, it is convenient to say that the SHPB test is still reliable for the performance of dynamic testing on soft specimens, especially polymeric based materials.

1.3 Static and dynamic mechanical behaviour of thermoplastic polymers

Thermoplastic polymers have been extensively used as engineering components that are purposefully designed to resist impact, ranging from bottles and pipes to helmets and body armours. Among the many types of thermoplastic polymers, polyethylene (PE), polypropylene (PP) and polycarbonate (PC) have attracted much interest from scientists as well as industry sectors. Based on this, many studies have been conducted to investigate their overall characteristics,

especially their mechanical performances (Li et al., 1995; Karian, 2003; Nitta and Maeda, 2010). Unfortunately, most of the previous researches were only focused on their static mechanical behaviour. Since the applications of these thermoplastic polymers have been extended from conservative to various engineering applications, the strain rate factor should not be neglected and requires extra precaution from the researcher.

Based on this consideration, some of the researchers have taken the initiative to experimentally investigate the mechanical properties of PE, PP, as well as PC at various levels of strain rates (Walley and Field, 1994; Mulliken and Boyce, 2006; Cao and Wang, 2012). Walley and Field (1994) reported that PE and PP show different patterns in terms of the rate sensitivity (i.e. maximum stress) as a function of the applied strain rate. It was experimentally proven that the PP specimen exhibits a bilinear relationship, where the rate sensitivity of stress increases sharply at a strain rate of about 10^3 s^{-1}. Conversely, the PE specimen does not unambiguously show a change of slope over a wide range of strain rates. Apart from that, Mulliken and Boyce (2006) found that the PC specimen shows a different magnitude of increment in terms of yield stress under both static and dynamic loading. They also reported that the slope of the yield stress increment is much greater under dynamic loading than that of static loading. Based on the recorded results, it is believed that the knowledge of the dynamic mechanical characteristic of these thermoplastic polymers (i.e. PE, PP, and PC) is still presently unclear. Therefore, it is believed that a more detailed and systematic study should be carried out in the future in order to achieve a conclusive explanation on the highlighted issues.

1.4 Static and dynamic mechanical behaviour of polypropylene based composites

In general, polypropylene (PP) is renowned as a high volume commodity plastic, with a remarkable cost/performance balance, which has contributed to its commercial success. Regrettably, this thermoplastic polymer is still referred to as a low cost engineering plastic and is inappropriate for crucial engineering applications. It is widely accepted that the incorporation of fillers into a PP matrix has shown great potential in increasing the longevity and durability of PP, fulfilling various requirements of engineering applications. For the past few years, many studies have been carried out on polypropylene-based composites using micro and nano-sized particulate reinforcement (Balasuriya et al., 2001; Alcock et al., 2007). They found that PP composites that are reinforced with nano-sized particles exhibit greater properties compared to their micro-scale reinforced counterparts (Jeong et al., 2005; Thostenson et al., 2005). Furthermore, it was also found that nanocomposites, with a good dispersion of fillers, show significant improvements in terms of their mechanical, thermal, electrical, optical, and physical-chemical properties, even at relatively low filler contents (Javni et al., 2002; Friedrich et al., 2005; Cho et al., 2006).

Zinc oxide (ZnO) and mica particles are promising fillers for reinforcing the PP matrix due to their outstanding properties as compared to other conventional fillers of a similar nature (Chiang et al., 2005; Cheng et al., 2007; Rashid et al., 2008; Rashid et al., 2011). Apart from that, it is believed that both composite systems have great potential as engineering products due to their capability to provide a good balance between impact resistance, production cost, and weight. Typically, the

majority of engineering products are mainly subjected to dynamic loading and therefore it is critical to investigate the dynamic behaviours of these two composite systems in order to avoid any mishaps during service. As with virgin polymers, existing works are highly focused on their static mechanical behaviour (i.e. PP reinforced with ZnO and mica particles). Unfortunately, the influence of fillers on strain rate sensitivity and the dynamic behaviour of both composite systems have often not been considered. This phenomenon might be attributed to the nature of the composite, which can complicate the specimen's geometrical design for dynamic testing (Hamouda and Hashmi, 1998). Nevertheless, several researchers have come out with an optimised specimen's geometry to overcome this drawback and claim that the dynamic facilities are also suitable and reliable for composite materials, especially polymer matrix composites (PMCs) (Hao et al., 2005; Guo and Li, 2007). Therefore, this is a great opportunity to discover the capabilities and possibilities of these composites to replace conventional materials, especially in dynamic loading applications.

1.5 Problem statements

It is generally acknowledged that the applications of thermoplastic-based products have been extended from conservative to more challenging applications like engineering components, constructions, load-bearing applications, etc. Hence, the strain rate effect should be the first priority factor to be investigated, since almost all of the highlighted applications are mainly involved with both static and dynamic conditions. In addition, the knowledge of rate sensitivity is also important during material selection in order to estimate the magnitude of changes in material's

properties. Without this knowledge, it is almost impossible to predict and prevent the unexpected failure during service. Recently, there is a very limited number of works that are concerned with the dynamic behaviour as well as the rate sensitivity of thermoplastic-based materials. In addition, numerical studies on the dynamic mechanical properties of these composites are also infrequently reported and need an additional effort to further clarify the relationship between the experimental and numerical results, which is important for engineering design and simulation purposes. Based on the highlighted issues, we believe that a systematic study is necessary to fulfil the lack of information in this area.

Apart from external factors like the strain rate effect, it was also believed that the internal structures of polymer (Liu and Baker, 1992; Wood-Adams et al., 2000; Wood-Adams, 2001) and the filler-matrix related characteristics of the polymer composites (i.e. as particle size, particle–matrix interface adhesion, particle shape and geometry) may also influence the mechanical properties of the polymeric specimens. However, we recognize that a similar kind of study under a dynamic range of strain rates has never been reported in the past and remains a major challenge in the development of a better understanding on the mechanical behaviour of thermoplastic-based products under various loading conditions.

1.6 Objectives of study

The objectives of this study are:

1) To compare the static and dynamic mechanical properties of several thermoplastic polymers

2) To examine the effect of molecular structures on the static and dynamic compressive properties of thermoplastic polymers.
3) To measure the static and dynamic mechanical properties of polypropylene based composites using nano and micro fillers.
4) To investigate the effect of particle size on the static and dynamic compressive properties of polypropylene-based composites.

1.7 Organisation of thesis

This thesis has been divided into altogether nine chapters. Each chapter gives the information about the research interest as mentioned in the objectives earlier.

- **Chapter 1** covers the introduction of the thesis. It contains a general overview on the development of static and dynamic testing and a brief introduction about dynamic studies on polymeric materials, a problem statement, objectives of the project and organisation of the thesis.

- **Chapter 2** contains some fundamental concepts of the split Hopkinson pressure bar technique, together with some reviews of related works reported in previous literature.

- **Chapter 3** explains the material specifications, research methodology, and experimental procedures which are carried out in this study.

- **Chapter 4** discusses the calibrations and verifications of the SHPB results.

- **Chapter 5** discusses the effect of the strain rate on several thermoplastic polymers (i.e. PE, PP and PC). In addition, in this chapter, the experimental results were also compared with two established equations namely the Eyring and power basic equations.

- **Chapter 6** discusses the effect of molecular structure on the static and dynamic compressive properties of the thermoplastic polymer, PE. As with Chapter 5, both the experimental and numerical results were validated using two established equations namely the Eyring and power basic equations.

- **Chapter 7** discusses the effect of the strain rate and particle content on the static and dynamic compressive properties of polypropylene-based composites (i.e. PP/nano-ZnO composites and PP/micro-Mica composites).

- **Chapter 8** discusses the effect of particle size on the static and dynamic compressive properties of polypropylene-based composites (i.e. PP/SiO_2 composites).

- **Chapter 9** concludes the findings of the project and the evaluation that has been made in order to assess the achievements of the objectives. Some of the suggestions for further study have been explained.

CHAPTER 2

LITERATURE REVIEWS

2.1 Introduction

This chapter summarises the principle of thermoplastic polymers followed by a brief overview of thermoplastic-based composites, explaining their increasing use in a wide range of engineering applications. In addition, a literature survey was carried out on the development of the dynamic facilities, especially a Split-Hopkinson pressure bar apparatus (SHPBA). Works on the static and dynamic behaviours of thermoplastic polymers and their composites were also extensively reviewed.

2.2 Polymers

Basically, the word polymer is derived from two different Greek roots which are ‘poly-‘, meaning many, and ‘mer’, meaning part or segment. Therefore, a polymer can be defined as the repetition of many similar segments (i.e. mer) that are connected together to form a long chain. In general, polymers are classified into three different classes which are thermoplastics, thermosets and elastomers (Harper, 2002). Among those classes, thermoplastic polymers have been widely used in both conservative and extreme applications.

2.2.1 Thermoplastic polymers

2.2.1.1 Characteristics of thermoplastics

A thermoplastic polymer usually begins in the form of a pellet, and then becomes softer (i.e. pliable and plastic) with increasing heat. As it cools, it will reversely transform back to the solid state without any cross-linked formation. This process (i.e. heating and cooling) can be repeated over and over, though continual recycling will ultimately degrade the polymer. In general, a thermoplastic polymer is subdivided into two distinct classes of molecular arrangement, which are semi-crystalline and amorphous as can be seen in Figure 2.1. These differences will significantly affect the behaviour of the thermoplastic material, especially during processing.

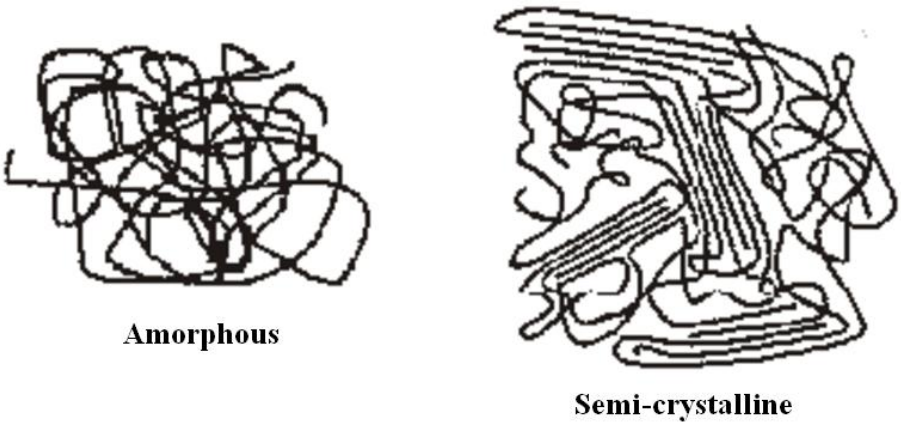

Figure 2.1: Molecular arrangement of amorphous and semi-crystalline thermoplastics (http://www.azom.com/article.aspx?ArticleID=83)

2.2.1.2 Semi-crystalline versus amorphous thermoplastics

Thermoplastic polymers like polypropylene (PP), polyethylene (PE), nylons (PA), polyacetal (POM), and thermoplastic polyesters (PET) are referred to as semi-crystalline thermoplastics where in the solid state, a great proportion of their molecular chains are structurally ordered and closely packed in certain specific

alignments. Meanwhile, polycarbonates (PC), polystyrene (PS), polyvinyl chloride (PVC) and acrylics (PMMA) are examples of amorphous thermoplastics. This indicates that in the solid state, their molecular chains are randomly arranged and this is attributed to the complex entanglement. It should be noted that at very high temperatures (i.e. melting state), both types of thermoplastic polymers will portray similar features of amorphous molecular structures. The key characteristics of semi-crystalline thermoplastics are translucent or opaque white colour, sharp melting point, good resistance to stress cracking and good fatigue resistance. Meanwhile, most amorphous thermoplastics tend to be naturally transparent, soften over a broad range of temperatures, prone to stress cracking and poor fatigue resistance. Table 2.1 shows the common examples for both types of thermoplastic polymers and their specific characteristics.

Table 2.1: Example of both semi-crystalline thermoplastics and amorphous thermoplastics and their characteristics (http://www.slideshare.net/Annie05/amorphous-and-semi-crystalline-presentation)

Amorphous high performance plastic		Semi-crystalline high performance plastic	
Key characteristics	Material	Key characteristic	Material
• High cost • Transparency • High strength • Good chemical resistance	- Polysulfone - Polyethersulfone -Polyetherimide	• High cost • Good toughness • High strength • Outstanding chemical resistance	- PEEK - PTFE
Amorphous engineering plastic		**Semi-crystalline engineering plastic**	
Key characteristic	Material	Key characteristic	Material
• Moderate cost • Good dimensional stability • Good optical qualities • Good impact resistance	- PC	• Moderate cost • Difficult to bond • Moderate strength • Good chemical resistance	- Nylon - UHMW-PE - Acetal
Amorphous commodity plastic		**Semi-crystalline commodity plastic**	
Key characteristic	Material	Key characteristic	Material
• Low cost • Bond well • Transparency	- PVC - Acrylic -Polystyrene	• Low cost • Good toughness • Low strength	- Polypropylene - Polyethylene

2.3 Composite material

A composite material is a material system that consists of two or more constituent materials with significant differences in terms of their physical or chemical properties, and which remain separate at the macroscopic or microscopic scale within the finished structure. The history of composite materials started in the early 20^{th} century. During that time, fibreglass was first introduced to reinforce several high performance thermoset resins, such as polyester and epoxy resins. After a few years, the composites industry evolved from thermosets to plastic resins in order to fulfil a wide range of light weight applications. It was reported that the earliest applications of glass fibre reinforced composite (GFRC) products were in the marine industry (Strong, 2002). In 1943, the first plane with a GFRC fuse ledge was flown at the Wright-Patterson Air Force base. Although this composite system was introduced almost seven decades ago but the GFRCs still dominate the recent composites market (i.e. covering approximately 90% of the composites market).

The rapid development of composite systems has revealed numerous types of newer and stronger reinforcements. Not only that, the alternative materials from metals and ceramics have also been manipulated as competitive matrix materials. To avoid confusion, composite families are divided into three distinct classes depending on the nature of their matrix. The most promising composites in recent industries is polymer matrix reinforced composites (PMCs). This composites system is based on the polymer matrix in either thermosets or thermoplastics. Although most of the PMCs are reinforced with fibre, but recently particulate fillers have started to gain much attention from researchers as well as industries. Other types of composites

systems are called metal matrix composites (MMCs) and ceramic matrix composites (CMCs) (Callister Jr, 1994).

2.4 Polymer matrix reinforced composites (PMCs)

According to Othman (2007), PMCs are classified into two major groups which are thermoplastics and thermosets. The thermoplastic group is subdivided into four other groups, i.e. glass mat, fibre reinforced, natural fibre thermoplastic composites and mineral reinforced thermoplastics. Meanwhile, the thermoset group is subdivided into two groups, i.e. carbon reinforced and natural/synthetic fibre reinforced. The detailed classifications of the polymer matrix composites are depicted in Figure 2.2.

A different classification of PMCs was made by Alger (1997). He classified PMCs into three major groups which are:

- Polymer-polymer combinations (i.e. polymer blends),
- Polymer-gas combination (i.e. expended, cellular or foamed polymers),
- Polymer-stiff filler combinations (i.e. polymer-fibre or polymer particulate composites).

Among these highlighted PMCs, the polymer-stiff filler combinations have attracted much attention from both researchers and industries due to their outstanding end properties.

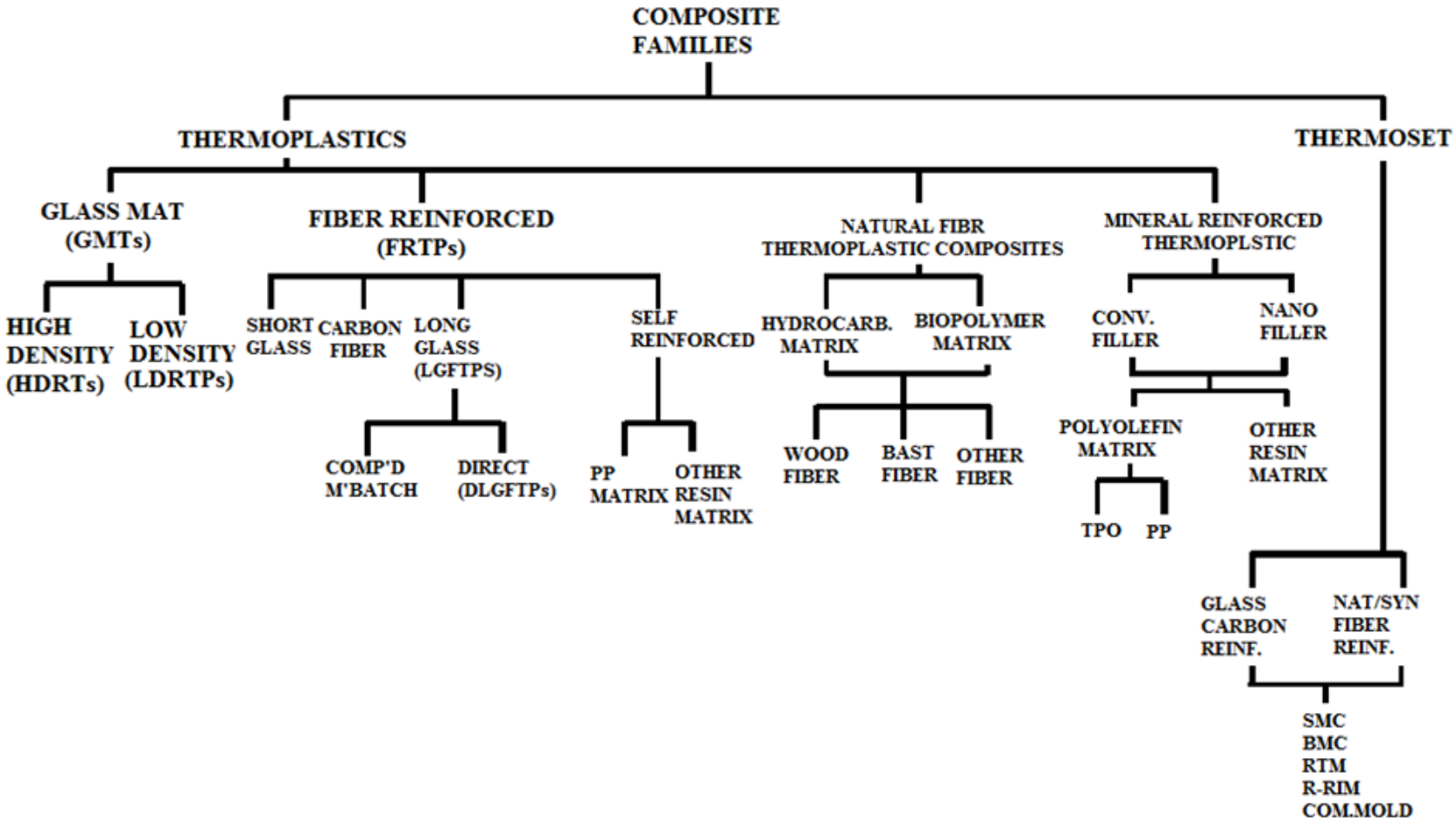

Figure 2.2: The classification of PMCs (Othman, 2007)

2.4.1 Benefits and drawbacks of PMCs

Polymer matrix composites (PMCs) offer a range of potential benefits over conventional neat polymers especially for high-end applications. The most common reason why PMCs are implemented in many critical applications like structural components is related with their capability to provide outstanding stiffness at lower weight than that of neat polymers (Callister Jr, 1994). Apart from that, other additional benefits offered by PMCs can be summarised as follows:

- Mechanical properties are outstanding
- Processing of PMCs does not involve high pressure and high temperature
- High abrasion resistance can be achieved
- Corrosion resistance is remarkable
- Low thermal expansion can be achieved
- Impact and damage tolerance characteristics are excellent
- Low production cost

However, it is important to realise that these highlighted benefits can be only achieved with the proper selection of the constituent materials and manufacturing techniques. Otherwise, the end results might be different or lesser. It is easy to be impressed with the potential benefits offered by PMCs but their drawbacks must also be considered. Normally, PMCs that contain natural fillers tend to absorb moisture, thus decreasing their overall performance, especially their mechanical properties (Dhakal et al., 2007; Mazuki et al., 2010). Apart from that, PMCs may also

encounter obscurity with a high coefficient of thermal expansion characteristic which results in dimensional instability. The anisotropic nature of PMCs may also contribute to difficulties in the design process (Mallick, 1993). In terms of their thermal resistance ability, PMCs show inferior performance at elevated temperatures. These disadvantages might restrict their utilization in some fields of application.

2.5 Particulate-filled polymer composites

As defined by the word "particulate", the reinforcing phase for this kind of composites are normally spherical or at least has dimensions of similar order in all directions (Lin, 2010). The introduction of particulate fillers into polymer matrices will significantly improve nearly every property of the virgin polymers, including their processing ability, dimensional stability, chemical resistance, strength, stiffness, etc. However, to achieve optimum properties, several factors should be considered carefully at the beginning stage of the filler selection. According to Rothon (2003), important filler characteristics such as cost, particle size, particle shape and geometry are the main elements that require extra consideration during the implementation of particulate fillers into a polymer matrix. Therefore, brief descriptions of each factor will be discussed in the following subtopics.

2.5.1 Cost

Initially, the main reason for using filled composites is to reduce the cost of the raw materials. It is generally known that the polymer is more expensive than the particulate filler. However, it is inappropriate to directly compare filled composites

with their raw materials in terms of cost saving criteria due to several principal reasons. Firstly, filled composites undergo more complex fabrication stages like the compounding process, which requires a bigger capital investment, more manpower as well as energy. Secondly, the prices of the raw materials (i.e. the filler and matrix) are normally quoted according to their weight, whilst those of their composites are based on their volume. Therefore, it will be more suitable if the comparison is made based on their cost-property performance, where the composite will definitely beat the original material (i.e. the filler and matrix).

2.5.2 Particle size

Particulate size is another factor that affects the end properties of filled composites. For synthetic fillers, the particulate size is highly dependent on the conditions during the synthesis process (i.e. precipitation) and possibly by any additional coating process. Meanwhile, for natural fillers, the particulate size is determined by the extraction process from the raw deposits, including the mining and separation stages. Until recently, numerous methods have been implemented to measure the particle size including optical scattering, diffraction from particulate suspensions and sieving.

Theoretically, particle size can be divided into three distinct categories namely primary particles, agglomerates and aggregates. The term “agglomerates” refers to a collection of weakly bonded particles, whereas the term “aggregates” refers to a collection of strongly bonded particles. For a better understanding of the

highlighted issues, Rothon (2003) has suggested an idealised view of particle types and their breakdown during the composite formation as illustrated in Figure 2.3.

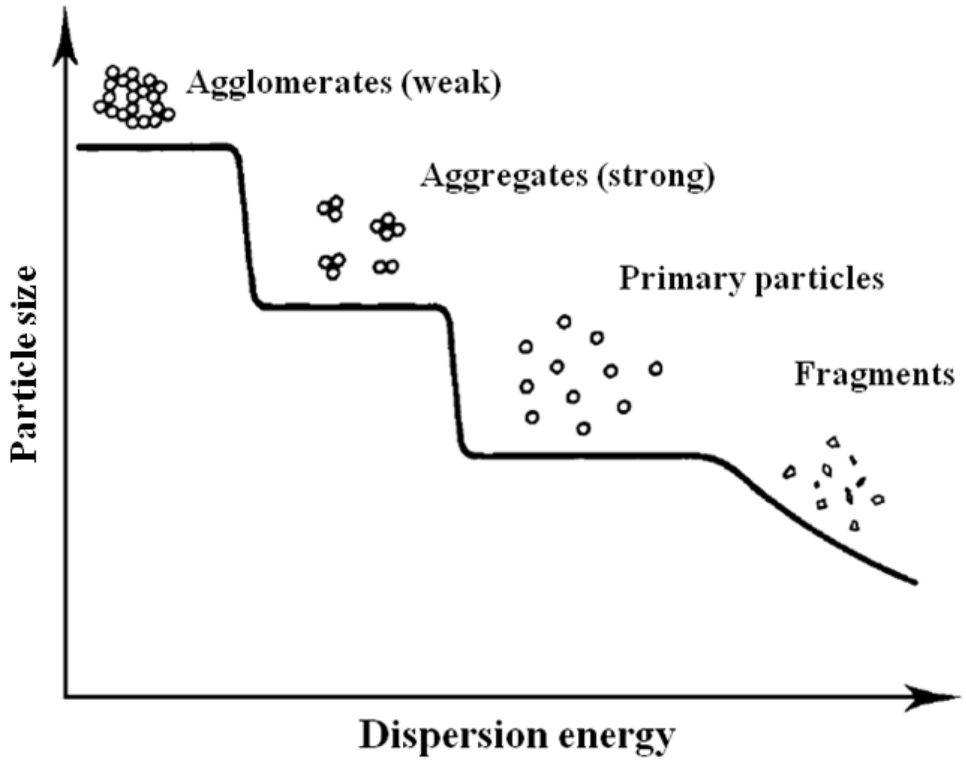

Figure 2.3: Idealised view of the way filler particles disperse and of the different forms of particle types that might be encountered (Rothon, 2003)

In most cases, filler systems do not follow the trend shown in Figure 2.3 where the steps shown are often less sharp and overlap. The majority of them exhibit more complicated profiles as depicted in Figure 2.4. From the recorded profile in Figure 2.4, it can be seen that those agglomerates, sometimes referred to as flocs, can arise due to the loss of colloidal stability in the polymerising systems, or to reticulation (filler network formation) above the glass transition, especially in cured elastomers, an effect often observed with carbon blacks. This phenomenon becomes more difficult and serious for synthetic products, especially those formed by

precipitation. For this kind of filler system, strong and complex aggregates are present. Normally, these aggregates will break down slowly and thus alter the ideal particle dispersion profile in Figure 2.3

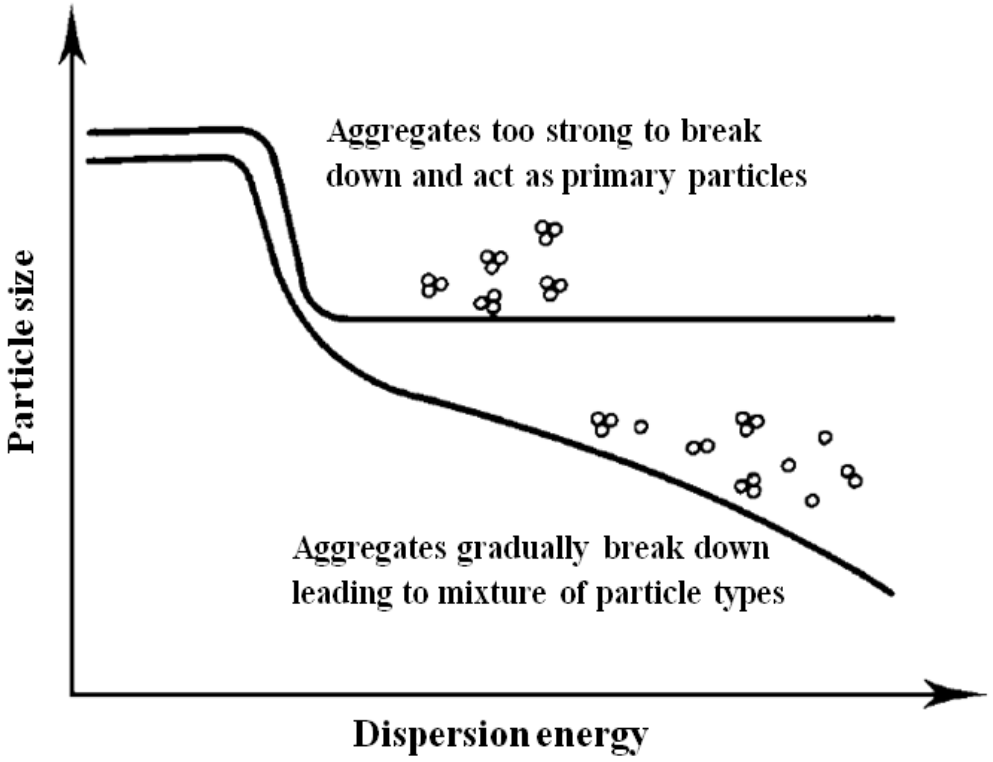

Figure 2.4: Complex particle dispersion behaviour, as often encountered with fine, precipitated fillers (Rothon, 2003)

2.5.3 Particle shape

As with particle size, the particle shape is an additional factor that influences the properties of the final product. The shape of the particle is often determined by the genesis of the filler, the crystal structure and processes it has undergone. Previous researchers have proposed several terms that describe the shape of a particle including spherical, flaky, platy, blocky, irregular, acicular, needle, etc. Therefore,

some typical particle shapes that are likely to be found in most particulate-filled composites are illustrated in Figure 2.5.

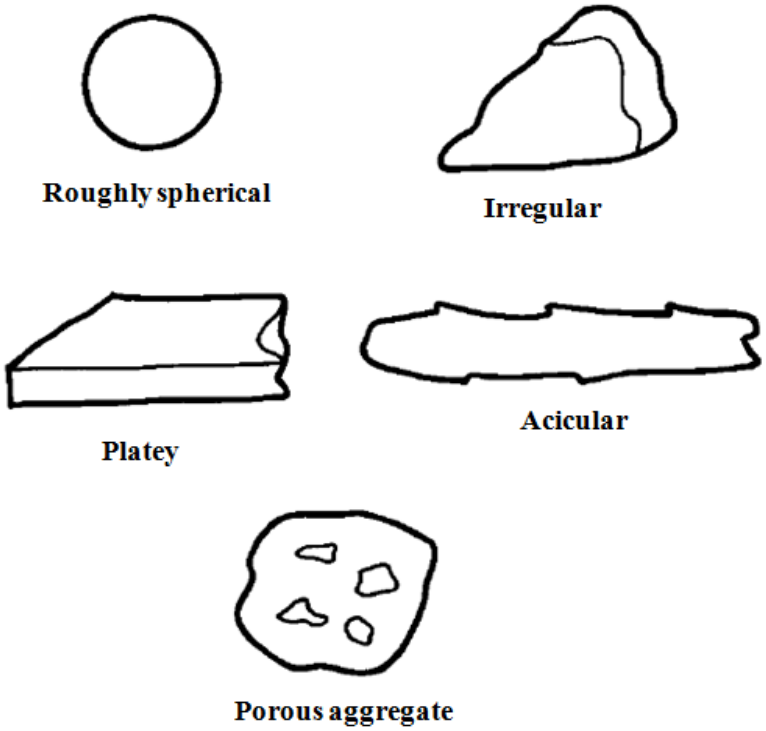

Figure 2.5: Some types of common particle shapes in particulate-filled composites (Rothon, 2003)

For synthetic fillers, their shape depends on both the production conditions and the chemical composition. For example, precipitated calcium carbonate ($CaCO_3$) can be produced in various forms including aragonite, calcite or vaterite by merely changing the precipitation conditions. These precipitation conditions can be manipulated (i.e. during drying and milling) to either produce single crystals or complicated aggregates. Meanwhile, the external shape of the mineral fillers is determined by their crystal structures as well as by the environmental conditions in which the mineral was formed. If permitted to grow without restraint, then the particle will be bounded by crystal faces in a regular way which is derived from

regular atomic arrangement. Nevertheless, under certain critical circumstances like under pressure, temperature or the effects of impurities, the crystal may adopt different shapes or habits such as cubic, fibrous (i.e. fine, long, needles), acicular (i.e. needle-like), lamellar (i.e. plate-like) and prismatic. Although, it is almost impossible to form perfect crystals, but even poorly formed ones will always show evidence of their intrinsic symmetry.

2.6 Particulate-filled thermoplastic composites (PFTCs)

As discussed in the previous section, thermoplastic polymers tend to soften appreciably as they are heated, thus decreasing their mechanical performance. Even worse, they start to lose their shape at elevated temperatures. Therefore, for the past few years, rapid and progressive efforts have been developed to overcome this dilemma. This can be seen in the early work on reinforced thermoplastic matrices by Leong and his co-workers (Leong et al., 2004b). Surprisingly, they found that the addition of mineral fillers (i.e. talc and $CaCO_3$) increases the modulus and crystallization temperature of unfilled thermoplastics.

The incorporation of mineral fillers including kaolin, talc, calcium carbonate and mica into thermoplastic polymers has become a common practice in the plastic industry. The main purpose for this kind of action is related to the cost reduction of moulded products. Apart from the cost reduction, fillers are also used to improve the mechanical properties of thermoplastics, such as strength, rigidity, hardness and durability (Katz and Milewski, 1987; Rusu et al., 2001; Chan et al., 2002). However, the optimum filler loading should be determined carefully since excessive fillers may

adversely affect the ductility, processability and strength properties of composites (Premalal et al., 2002; Fu et al., 2008). Lately, PE and PP are the most popular semi-crystalline thermoplastic polymers to be used as matrices in compounding with fillers. Meanwhile, polystyrene (PS) and polycarbonates (PC) have recorded a similar popularity trend for amorphous thermoplastic polymers.

Many studies have been demonstrated on particulate-filled polyethylene composites in order to fully characterise their overall performance. As pointed out by Zhao et al. (2005), the strength and modulus of PE/clay composites have been found to increase perpendicularly with increasing clay loading, whereas the notched impact strength shows a contrary trend. In addition, the thermal stability of PE/clay composites is far better than that of unfilled PE up to certain clay loadings. It is believed that organoclay can play two conflicting functions in the thermal stability of polymer/clay nanocomposites. At low clay loading, the clay layers become effective barriers, thus significantly increasing the thermal stability of the PE/clay composites. However, with increasing clay loading, the catalysing effect rapidly rises and becomes dominant, so that the thermal stability is decreased. The addition of metallic filler into the PE matrix is believed to increase the thermal conductivity properties of the neat PE as previously reported by Kumlutas et al. (2003). They proved that the addition of conductive particles (i.e. aluminium) into the HDPE matrix gradually increased the thermal conductivity of the composites as compared to unfilled HDPE.

Another common commodity plastic is PP. Progressive attention has been specifically made in order to extend its applications from conservative to more challenging applications. For this reason, several researchers have been intensively

involved in works that are related with reinforced PP. For example, Svoboda et al. (2001), reported that the presence of clay filler increases the tensile modulus but decreases the elongation up to a certain extent. Typically, the pure PP and the PP/clay composites with a low clay content exhibit yielding behaviour in the stress-strain characteristic with a maximum elongation of up to 200%. Meanwhile, PP/clay composites that had been reinforced with a clay content higher than 7% did not show any yielding behaviour, where samples were immediately broken after reaching the maximum loading (i.e. stress). More recently, a study by Manchado et al. (2005) investigated the effect of different fillers (i.e. single-walled carbon nanotubes and carbon black) on both the thermal and mechanical properties of reinforced PP composites. Initially, it was found that the introduction of both reinforcements significantly increased the Young's modulus of the composites up to a certain extent. However, the increment trend was somehow different between these two fillers. They mentioned that a further increase in single-wall carbon nanotubes proportion in the composites (i.e. 1 wt %) provided a marked decrease in the tensile modulus, whereas carbon black fillers recorded an increment pattern with increasing filler content. The difference is mainly attributed to the morphology of both fillers. For a similar interface area, carbon blacks with more isometric particles may induce a significant difference in their aspect ratio, meaning that the former are able to entangle and interconnect more easily and more often than that of the latter. Meanwhile, increasing the single-walled carbon nanotubes concentration in the composites may encourage the formation of aggregates. It is assumed that the aggregates of nanotube ropes will significantly reduce the aspect ratio (length/diameter) of the reinforcement, hence reducing the rigidity of the composites.